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DIRECT CATALYTIC DECOMPOSITION OF NITRIC OXIDE

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MASTER

Project Title: DIRECT CATALYTIC DECOMPOSITION OF NITRIC OXIDE

Abstract

This project investigates a suitable catalyst system for the direct NO decomposition in post-combustion NO_x control. The process does not use a reductant, such as the ammonia used in the case of Selective Catalytic Reduction (SCR) of NOx to nitrogen. Therefore, it is a greatly simplified process basically involving passing the flue gas through a catalytic converter.

Catalysts are prepared by incorporating metal cations into zeolite supports according to ion exchange procedures widely used in preparation of metal/zeolite catalysts. The catalysts of primary interest include copper, palladium, silver, and nickel exchanged zeolites. Particular emphasis is given in this work on promoted Cu-exchanged zeolites, especially the catalyst system Mg/Cu-ZSM-5 and a few others, which are promising for NO conversion to nitrogen at typical flue gas O_2 and NO levels and over the temperature range of 723-873K. Effects of zeolite modification, copper exchange level and catalyst preparation conditions on the catalyst activity are studied in a packed-bed microreactor. Temperature-programmed desorption (TPD) and reduction (TPR) experiments will be carried out in a thermogravimetric analyzer and a single-particle electrodynamic balance (EDB). Kinetic studies of NO and O_2 interaction with catalysts over a wide temperature range as well as catalyst structural investigations are planned.

PROGRESS SUMMARY

Catalyst Synthesis and Characterization

During this quarter, 15 catalyst samples, listed in Table 1, were prepared by exchanging metal cations, $Cu^{2+}/Mg^{2+}/Zn^{2+}$, into the Na-ZSM-5 zeolite substrates. The exchange procedures are briefly described below. For the catalysts #7-#9, the Na-ZSM-5 was ion-exchanged in a solution of copper (II) acetate with concentration of 0.5 mmol/dm^3 and with ammonia addition (at a ratio of $NH_4^+/Cu^{2+}=0.5$) at 50°C overnight, and separated from the solution by filtration. The obtained wet cake was again ion-exchanged in a new copper(II) acetate and ammonia solution. After 3 time repeats of the ion exchange treatment, the sample was washed in deionized water and dried at 110 °C overnight. For the remaining of Cu exchanged zeolite catalysts, the preparation procedure was the same as that for catalysts #7-#9, except no ammonia was added in the solution. For Mg/Cu-exchanged zeolites, the Na/ZSM-5 zeolites were ion-exchanged with Mg^{2+} in a $Mg(NO_3)_2$ solution with concentration of 0.3 - 0.8 mmol/dm^3 at 90°C for two hours first. The Mg exchange level was about 50% in the obtained zeolites. After the Mg^{2+} exchanged zeolites were seperated from the solution by filtration, the samples were ion-exchanged overnight with Mg^{2+} and Cu^{2+} cations simultaneously in $Mg(NO_3)_2$ and $Cu(OOCCH_3)_2$ solution, in which $Mg(NO_3)_2$ and $Cu(OOCCH_3)_2$ concentrations were about 0.3-0.8 mmol/dm^3. Since Cu cations are easier to exchange Na^+ in Na-ZSM-5 than Mg cations(1), it is hard to get high Mg loading in ZSM-5 according to the above technique. We will continue to work on this by modifying our exchange procedure. All samples were characterized by Plasma Emission Spectrometry (ICP) (Perkin-Elmer Plasma 40) to measure contents of metal cations exchanged into the zeolites after dissolving samples in an HNO_3 solution and by checking the aqueous metal cation solutions before and after the exchange step. The Cu^{2+} exchange levels range from 73% to 150% in the Cu^{2+}- exchanged zeolites, while Mg^{2+} exchange levels of 0.6% to 11% and Cu^{2+} levels of 50% to 72% were measured in Mg^{2+}/Cu^{2+}-exchanged zeolites. The high Mg loading of catalyst #16 resulted from impregnation using a concentrated(85 mmol/dm^3) $Mg(NO_3)_2$ solution. The Zn^{2+} and Cu^{2+} exchange levels are 76.6% and 44.5%, respectively, in the Zn^{2+} and Cu^{2+} co-cation exchanged zeolite. For catalysts #20 and #21, different parent zeolites were used, namely 881027b ZSM-5 and high Si/Al ratio ZSM-5 supplied, respectively, by Dr. Patric Voogd of Delft University of Technology, the Netherlands and Davison Co., with respective Si/Al ratio of 90 and 320. The ICP was recalibrated after an error had been found. This error affects the previously reported measurements. A corrected Table 2 from the 3rd Quarterly Report(2) is provided in the appendix.

The new catalysts are used to test the effects of copper exchange level, promoter cations and acidity (Si/Al ratio) of the parent zeolites on the catalytic activity.

Experimental

Continued testing of the catalysts prepared during the last and this quarter was performed to study the effects of Cu^{2+} exchange level and the promoting effect of Mg^{2+} on the catalytic activity of ion exchanged zeolites. Comparisons of NOx analyzer and GC measurements were made to check their agreement. The experimental conditions used this quarter are the following: reaction temperatures 350- 600°C, contact time 1-4g s/cc(STP), NO concentration 0.2%-4%, and O_2 concentration 0%- 0.61%. The heat pretreatment of catalysts for catalytic activity measurements consisted of heating the catalyst in He at 500°C for two hours. Long-term tests of catalyst activity were performed with catalyst #4. The decomposition of NO_2 was also examined this quarter over catalyst #4.

Results and discussion

In previous work, we mainly used a NOx chemiluminescence analyzer to monitor concentrations of NO and NOx down stream of the reactor. The difference between the NO and NOx measurement is due to NO_2 formation. This quarter, a gas chromatography with a thermal conductivity detector was also used to check O_2 and N_2 formation. A molecular sieve 13X column(1/4" I.D. x 6ft long) was used in the GC. The NO conversion into O_2 and N_2 was determined by (O_2 or N_2 concentration in exit gas)/ (1/2* NO concentration in inlet gas stream).

GC measurements and NOx analyzer measurements were compared for measurement consistency. Fig.1 shows that conversions calculated based on NO, NOx measurements from the NOx analyzer, and O_2, N_2 measurements from the GC over catalyst #4 at a contact time of 4g s/cc and 2% NO in the gas were in good agreement. When the contact time was decreased to 1g s/cc, and NO concentration to 0.2%, NO conversion to N_2 computed from the GC and NOx analyzer measurements were almost the same over whole temperature range. These results are shown in Fig.2.

However, variations between NO conversion and O_2 and N_2 formation are typically reported in the literature, when using gas chromatography data alone. The reason for this is that NO_2 is homogeneously produced in the cool parts of the reactor discharge system by the reaction of unconverted NO with produced O_2 (3, 4). When NO conversion to N_2 is high, the concentration of the unreacted NO in the exit stream is low. Therefore, NO_2 formation decreases as NO conversion to N_2 increases. Also low levels of NO_2 were measured when the initial concentration of NO was low(e.g. Fig.2).

The effect of contact time on the NO conversion to N_2 and O_2 over catalyst #4 was examined by the GC with a gas containing 4% NO at a temperature of 450 °C. As we reported before (2), NO conversion measured by the NOx chemiluminescence analyzer increased with the contact time . Our GC measurements presently show that the O_2 and N_2 products increase with the contact time, as can be seen in Fig. 3. However, there exists a difference between NO conversion to N_2 and between N_2 and O_2 produced, simlilar to what has been reported in the literature (3, 4) in the temperature studies of Cu/ZSM-5 catalysts. At the temperature of 450°C, studied here, no N_2O is formed. The difference, then, is attributed to NO_2 production. This is almost constant over the studied range of contact time. At low contact time, the concentration of unreacted NO is high, whereas the residence time of NO and O_2 in the reaction system is short. At high contact time, the NO concentration in the exit gas stream is low, but the residence time of gas reactants is long. Combined, the effects of the NO + O_2 reaction rate and the product gas residence time make the NO_2 formation approximately the same.

Mg^{2+} cations were found to promote the catalytic activity of Cu^{2+}-exchanged ZSM-5 when O_2 was present in the feed stream. Fig.4 shows NO conversions to N_2 over catalyst #4 at a contact time of 4g s/cc without O_2 and with 0.61% O_2 in the inlet stream. It is clearly seen that the oxygen presence in the feed gas stream did not reduce the catalytic activity of this Mg^{2+}/ Cu^{2+} co-cation exchanged sample. However, the catalytic activity of Cu^{2+} exchanged ZSM-5 decreases when O_2 is present in the reactor feed gas. Figure 5 shows this for catalyst #6 for NO decomposition with or without O_2 in the He+ NO stream.

The catalytic activity of Cu^{2+}/Mg^{2+} ion exchanged zeolites did not deteriorate over long term run. Figure 6 is a test result over six days of NO decomposition into N_2 over catalyst #4 at 4% NO concentration and 450°C.

Our GC measurements have confirmed that the inlet NO concentration doesn't affect the NO conversion much when the inlet NO concentration is above 0.5% (2). The results of NO conversion into N_2 over catalyst #6 at 2% and 4% of NO concentrations are shown in Figure 7. The NO conversions are same over temperature ranging from 350 to 600°C.

Mg^{2+}/Cu^{2+} co-cation exchanged ZSM-5 is active for NO_2 decomposition to NO and O_2. A preliminary run of direct decomposition of NO_2 over catalyst #4 was performed, and results are shown in the Fig. 8. The NO_2 conversion was higher than 75% over temperature range of 350 to 600°C.

Plans for Next Quarter

Testing of Cu^{2+}/ZSM-5 catalysts promoted with cations, such as Mg^{2+}, Zn^{2+}, Ag^{2+}, and Pt^{2+} will be conducted to examine what role these cations play in the NO decomposition in the zeolite catalysts. The effect of acidity of parent ZSM-5 on the catalytic activity will be tested at various conditions. Titration of the acid sites in the ion exchanged ZSM-5 is planned to determine whether the number of copper and other cations correlate with the available acid sites in the zeolite sample.

References

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Table 1. Cation Exchanged Zeolites[#]

Catalyst Number	Si/Al	Cu Exchanged level (%)	Mg Exchanged level (%)	note
7	21.5	113		a
8	21.5	108		
9	21.5	99		
10	21.5	50	5	
11	21.5	53	5.2	
12	21.5	150		a
13	21.5	72	11	
14	21.5	73		
15	21.5	67.2	0.6	
16	21.5	14	490	b
17	21.5	145		
18	21.5	44.5	Zn=76.6	c
19	21.5	N/A		a
20	90	82		
21	320	64		

Zeolites: Na-ZSM-5(low ratio: Si/Al=21.5, and high ratio: Si/Al=320) supplied by Davison; Catalyst #20 with Si/Al=90 was prepared at Delft University of Technology, The Netherlands.

a. CuO particle formation indicated by color change.

b. Mg was put into zeolite by impregnation method.

c. Zn cation exchanged instead of Mg.

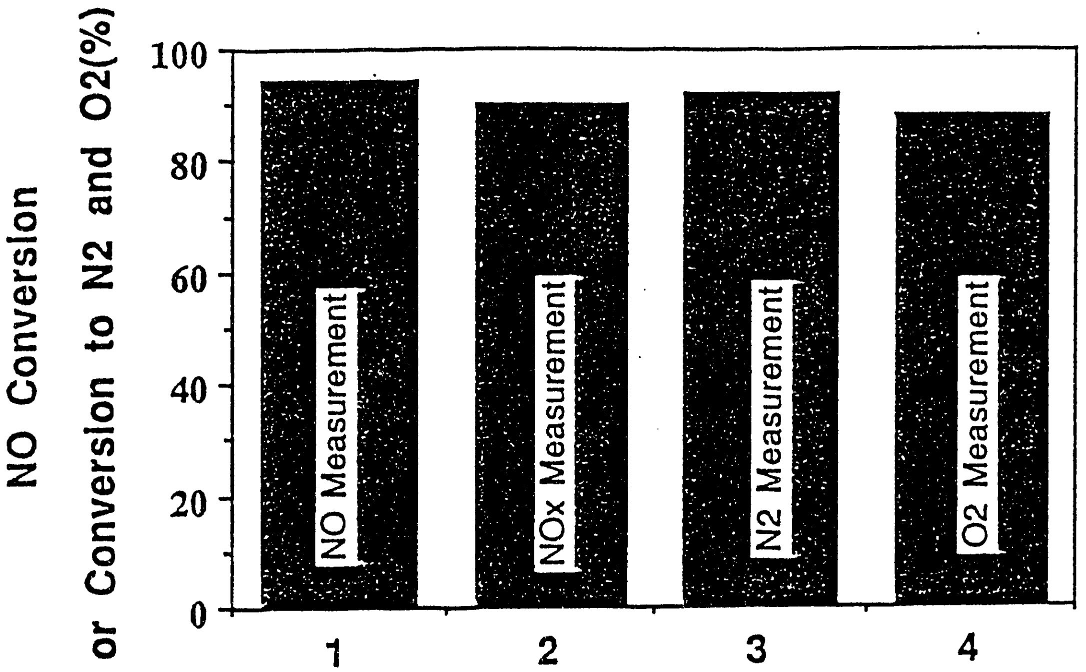

Fig.1 Comparison of NOx analyzer and GC measurement for NO decomposition over catalyst#4[Mg(11%)/Cu(119%)-ZSM-5] at 450°C reaction temperature, 2% NO-He and contact time, W/F=4g s/cc.

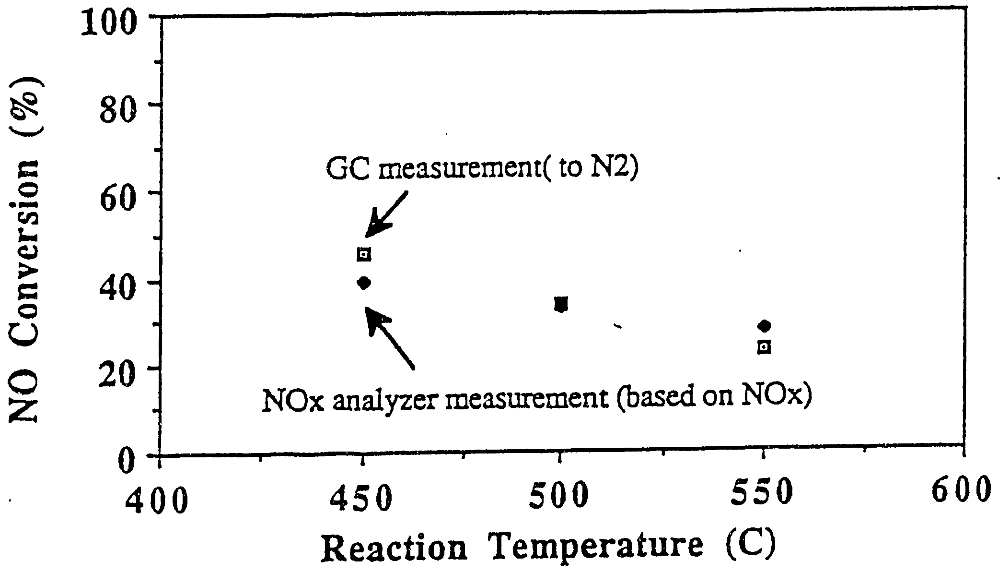

Fig.2 NO decomposition over catalyst #4 at 0.2% NO-He, and W/F=1g s/cc.

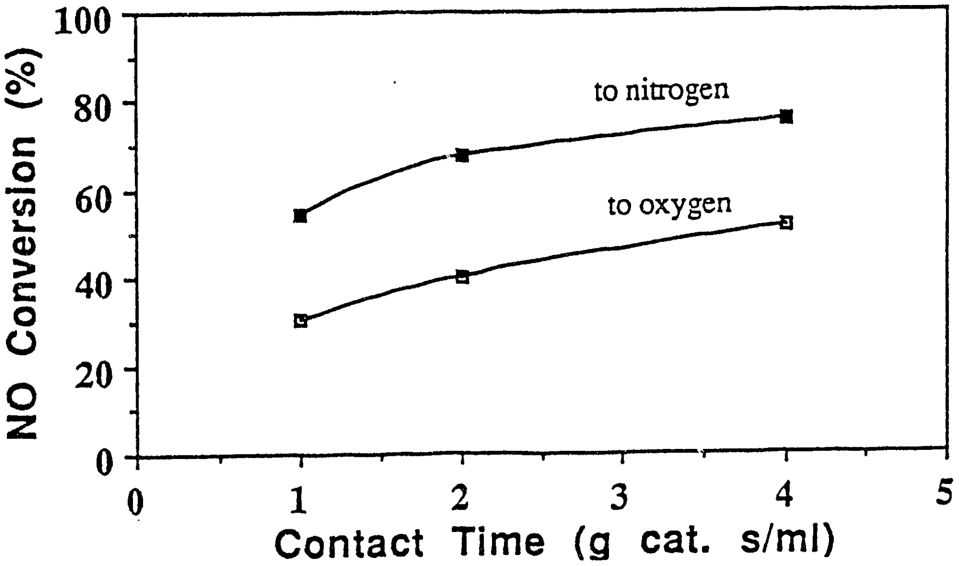

Fig.3 Effect of contact time on NO conversion over catalyst #4 at 450^{o}C and 4% NO-He.

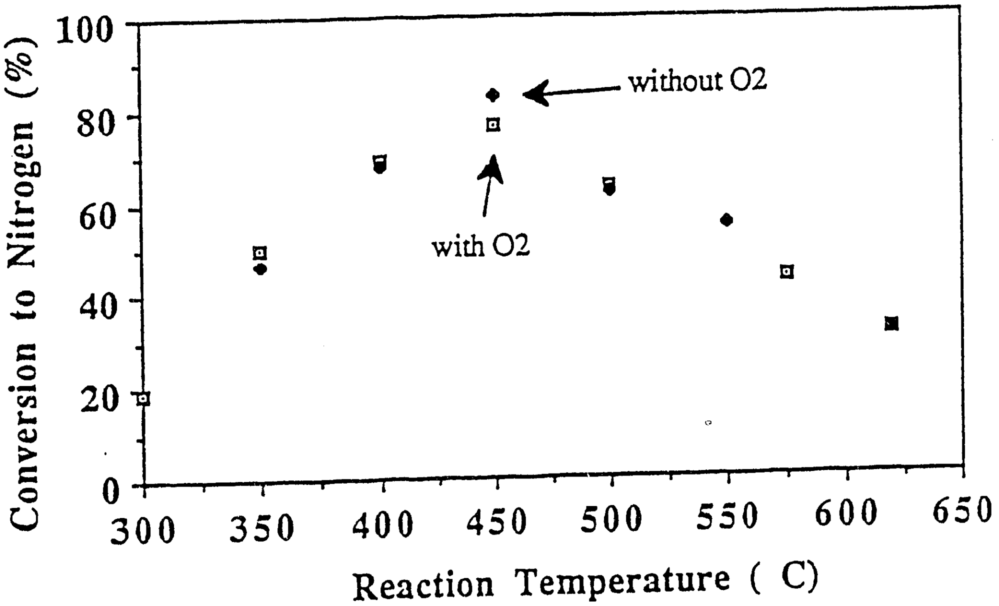

Fig.4 Effect of O_2 present in feed gas on NO decomposition to N_2 over catalyst #4 with 2% of NO and a contact time of 4g s/cc (◆ - without O_2, ⊡ -with 0.61% O_2).

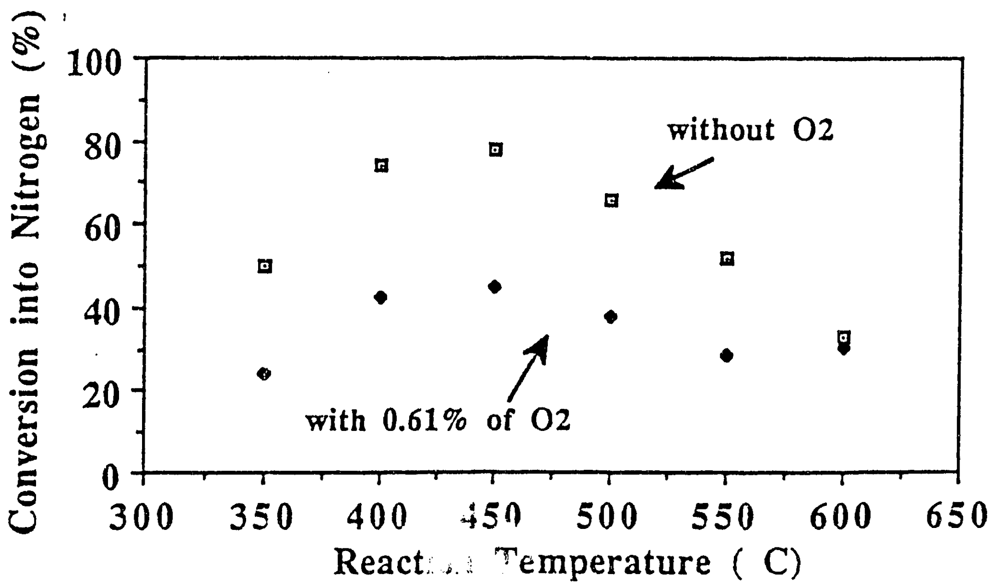

Fig.5 Effect of O_2 present in feed gas stream on NO conversion to N_2 over catalyst #6[Cu(108)/ZSM-5] with 2% NO-He and a contact time of 4g s/cc(▣ - without O_2, ◆ - with 0.61% O_2).

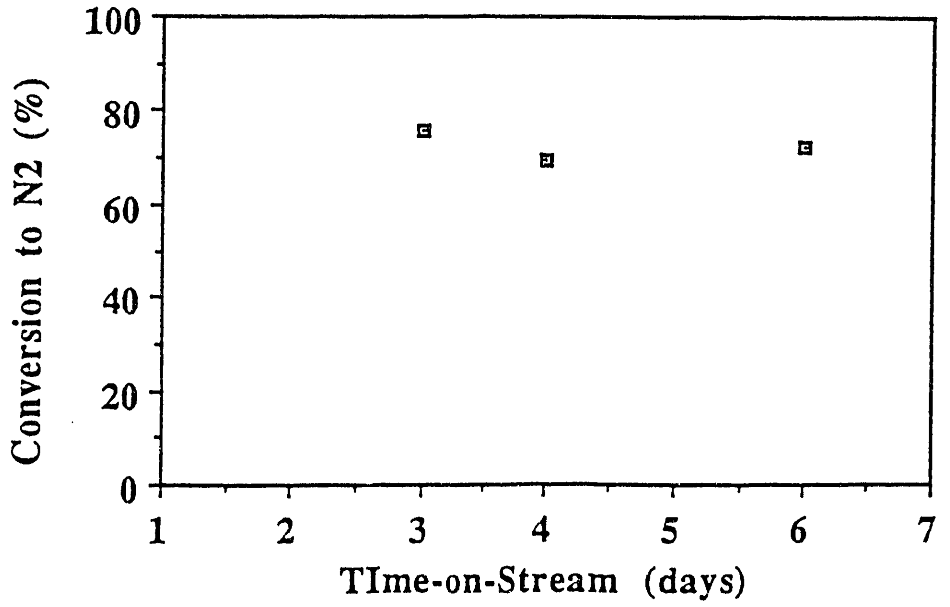

Fig.6 Long-term activity of catalyst #4 as a function of reaction time at 450°C temperature, 4% NO-He and a contact time of 4g s/cc.

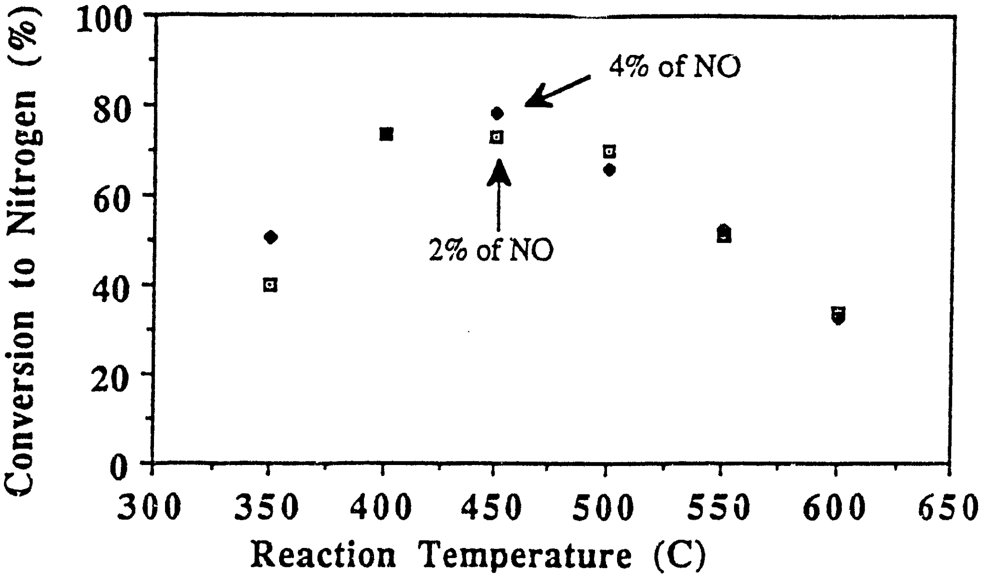

Fig.7 Activity of catalyst #6 at a contact time of 4g s/cc and different NO feed concentrations.

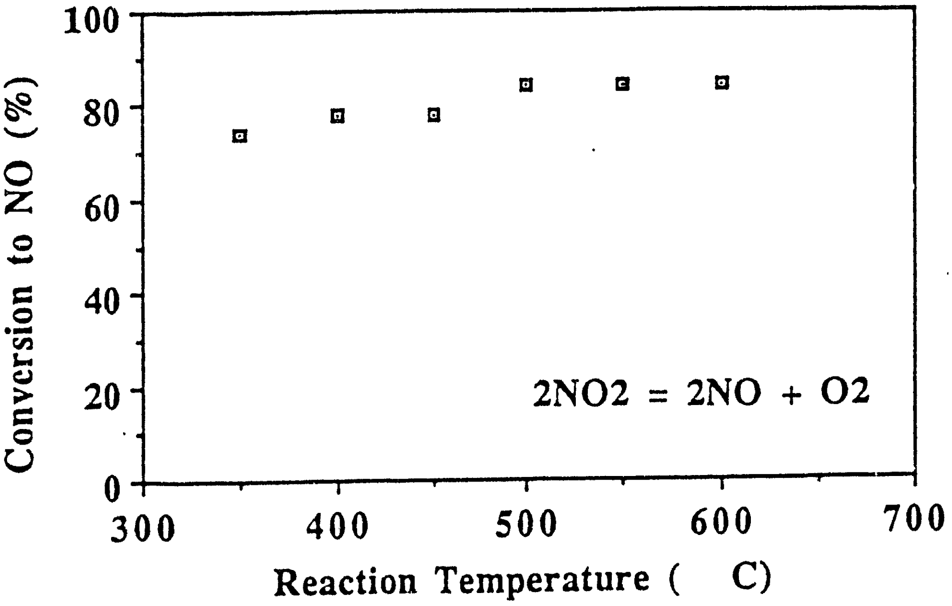

Fig.8 NO_2 decomposition over catalyst #4 as a function of reaction temperature at 467 ppm of NO_2-He and a contect time of 2g s/cc.

Appendix

Table 2. Summary of Cation Exchange Levels of Catalysts

Catalyst Number	Cu^{2+} in Solution[a] (ppm) ICP	AA	Mg^{2+} in Solution (ppm) ICP	Catalyst Weight (g)	Exchange Level (%) Cu^{2+}	Mg^{2+}
1	10.1	10.8		0.10366	96.7 (103)[d]	
2[b,c]	10.8	11.43		0.10185	N/A	
	11.5	12.2		0.10644	N/A	
3	11.6	12.3		0.10496	101 (107)	
4	10.7	11.4	0.2	0.10459	112(119)	11
5	9.4	10.0	0.1	0.10500	88(93)	5.6
6	9.0	9.5	0.1	0.09892	89(93.9)	5.9

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a. 203 ml of 1% HNO_3 solution

b. no Si/Al data available at this point

c. data in second line for catalyst #2 calcinated in air at 500°C for 2 hours

d. data in parenthesis calculated from AA measurements

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